

Physically meaningful solutions of optimized effective potential equations in a finite basis set within KS-DFT framework

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The numerical evidence is provided showing that the physical solutions, in a finite basis set, of the optimized effective potential equations (OEP) in the context of the Kohn-Sham Density Functional Theory (KS-DFT) can only be obtained by employing the proper regularization procedure in the OEP method together with a judicious choice of basis sets used in the KS OEP calculations. The regularisation relies on the truncated singular value decomposition procedure to obtain the pseudoinverse of the density-density response matrix. We are showing that this is a critical aspect in determining the stable and numerically accurate solutions of the KS-OEP equations for the exchange-only and correlated cases.

I. INTRODUCTION

There has been a strenuous interest in using the orbital-dependent exchange-correlation functionals in the context of the Kohn-Sham (KS) density functional theory (KS-DFT)[1–19], since they have proven to provide a systematic way to overcome the limitations of conventional density-dependent approximations [20] such as the presence of self-interaction error, qualitatively incorrect exchange, and correlation KS potentials,[21, 22], description of dispersion interactions [23, 24] and the KS occupied-virtual energy-gaps.[25, 26]. In addition to providing one of the most effective tools to develop accurate XC KS-DFT potentials and functionals, they are also emerging as an appealing tool for computational chemistry studies.[27–30] Nevertheless, the use of explicit orbital-dependent functionals within the KS scheme is significantly hindered by the fact that the KS orbitals cannot be expressed directly as the function of the electron density. For this reason, in the true self-consistent KS scheme, the optimized effective potential (OEP) method must be employed,[31] to determine the associated local XC potential, which is formally defined as the functional derivative of the XC functional $E_{xc}[\rho]$ with respect to the electronic density $\rho(r)$. For the exchange-only case, the method has a long history, starting by Sharp and Horton [32] to determine a multiplicative exchange potential variationally, followed by practical realization proposed by Talman and Shadwick [33], and it is identified as the exact exchange-only KS (EXX or OEPx) potential. The OEPx method is exactly defined in terms of occupied KS orbitals[1–4, 34, 35]. Many OEPx approaches with different efficiency, accuracy or numerical stability have been presented in literature [34–48], followed by practical applications for both molecular [29] and solid-state systems.[28, 30] The OEPx method possesses many important features, e.g., it removes the one-electron self-interaction error, its exchange potential

has a correct $-1/r$ asymptotic behavior [33], is exact in the homogeneous-electron-gas limit exhibits an integer discontinuity[49–51] upon addition of an infinitesimal fraction of an electron to the highest occupied orbital and obeys the exchange virial theorem[52, 53], and then improves many other KS quantities [3, 4, 7, 29, 34, 35].

For the correlation functional and fully self-consistent correlated KS-OEP calculations, usually, the perturbation theory is involved, most cases are restricted to the use of second-order correlation. In such a case, the most straightforward choice is the utilization of energy expression from the second-order Görling–Levy perturbation theory (OEP-GL2)[54], which has the same form as a functional defined from the many-body perturbation theory (MBPT)[6, 55]. Alternatively the random-phase-approximation correlation can be used[14, 17, 48, 56, 57]. The most successful forms of the KS-OEP correlation functionals have emerged from the *ab initio* DFT approach of Bartlett et. al. [6, 8, 58] in which the OEP correlated energy expressions are based on many-body coupled-cluster and perturbation theories and are applied to the KS system so that the systematic improvement can be achieved, in analogy with wave-function-based methods. Among the second-order *ab initio* DFT approaches, the OEP2-sc [8] method has proven to be one of the most stable, providing very good results in many investigated cases [8, 22, 59–63]. It provides reasonable correlation and total energies, correlation KS-OEP potentials and relaxed electron densities, correctly describes self-interaction, has the correct long-range behavior and provides good ionization potentials and excitation energies [59]. Most of the quantities obtained from OEP2-sc calculations are often better than the corresponding *ab initio* second-order Moller-Plesset (MP2)[64] and even coupled-cluster singles and doubles (CCSD)[65] and certainly much better than the ones obtained using the existing standard density-dependent DFT functionals[22]. On the contrary, the OEP-GL2 approach leads to a large overestimation of correlation effects[6, 8, 66–68], like correlation energy, correlation potentials, or even correlated density, and undoubtedly causes a problem with convergence in many cases. [8, 22, 60, 61, 63, 69, 70] As an

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alternative to the OEP2-sc methods, the spin-resolved (SR) modification of the OEP-GL2 method [70] can be used to improve the OEP-GL2 performance[70–73].

This makes us understand that the KS-OEP method depends on the efficient approach for solving OEP integral equations. The numerical grid-based concept can be used, but with limitations to the atomic and molecular systems with high symmetry. In practical realization, to ensure that KS-OEP calculations can be made in the standard Gaussian basis sets for quantum chemical applications, the linear combination of atomic orbitals (LCAO) OEP method is used [34, 35]. The finite basis set implementation of the OEP approach incorporates a projection method[35, 74] for solving the required integral equation, and by construction, all potentials could be expanded in terms of auxiliary Gaussian functions. Some computational difficulties have been faced in the application of the LCAO OEP calculations, both to the exchange-only energy functional[31, 41, 42, 45, 75–81] and with correlation included[60, 82, 83] which is a usual manifestation of the well-known instability associated with numerical solutions of Fredholm integral equations of the first kind. [84]In order to obtain numerical solutions of reasonable accuracy for this class of equations (KS-OEP), cautious selection of Gaussian basis sets is required, and what is even more important is the utilization of the proper regularization techniques in obtaining the inverse of the density-density response matrix in the OEP procedure. Previous experience has shown that the use of the same basis set to represent both the orbitals and potentials is desirable and that the uncontraction of the basis set often minimizes numerical difficulties.[8, 31, 60, 61, 74] These issues have been discussed extensively in the literature and several schemes have been proposed for managing this problem.[41, 42, 45, 75–82, 85] In addition, for correlated OEP calculations, such as those considered in this work, we must take care to ensure that the basis sets used are suitable for the description of correlation effects akin to those employed in standard wave function-based calculations.

Mixing the problems mentioned above of solving the OEP equations, with the convergence issues in the case of OEP-GL2 for some atomic and molecular systems [66, 68, 86, 87], together with the wrong choice of Gaussian basis sets and the underestimation of the use of the regularization procedure[82], introduces some confusion in the context of the application of KS-OEP methods. Therefore it still affects the lack of confidence in implementing the KS-OEP methods and then in the quality of the results. In this study, we provide numerical evidence that the physically meaningful solutions of the KS-OEP equations on a finite basis can only be obtained by employing the proper regularization procedure in the solution of the OEP equations.

II. THEORY

In the KS-OEP method, the KS XC potential $v_{xc}^{OEP} = \delta E_{xc}/\delta \rho$ corresponds to a given orbital-dependent energy expression $E_{xc} = E_{xc}[\{\phi_{p\sigma}\}, \{\varepsilon_{p\sigma}\}]$, where $\{\phi_{p\sigma}\}$ and $\{\varepsilon_{p\sigma}\}$ are sets of KS orbitals and eigenvalues, respectively, obtained through the self-consistent solution of the KS equations

$$\left[-\frac{1}{2}\nabla^2 + v_{s,\sigma}(\mathbf{r})[\rho]\right] \phi_{p\sigma}(\mathbf{r}) = \varepsilon_{p\sigma} \phi_{p\sigma}(\mathbf{r}), \quad (1)$$

with the local effective KS potential

$$v_{s,\sigma}[\rho](\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_J(\mathbf{r}) + v_{xc,\sigma}(\mathbf{r}), \quad (2)$$

where v_{ext} is the external (nuclear) potential, v_J is the classical Hartree potential and

$$\rho(\mathbf{r}) = \sum_{\sigma} \rho_{\sigma}(\mathbf{r}) = \sum_{i,\sigma} |\phi_{i\sigma}(\mathbf{r})|^2 \quad (3)$$

being the electron density. All through this section, we use the convention to label with σ the spin degrees of freedom and with i, j the occupied KS orbitals, with a, b the unoccupied ones, with p, q, r, s the general (occupied or unoccupied) ones. It is useful and a common practice in orbital-dependent approaches to divide the XC energy functional as $E_{xc} = E_x + E_c$, separating the exchange and the correlation contributions. The exchange energy functional has the form of the usual Hartree-Fock exchange energy

$$E_x[\{\phi_{q\tau}\}] = -\frac{1}{2} \sum_{\sigma} \sum_{ij} (i_{\sigma} j_{\sigma} | j_{\sigma} i_{\sigma}), \quad (4)$$

with $(p_{\sigma} q_{\sigma} | r_{\sigma} s_{\sigma})$ being two-electron integrals in the Mulliken notation computed from KS orbitals.

For the correlation part, we will limit ourselves to the *ab initio* DFT functionals and expressions obtained from the second-order Görling–Levy perturbation theory (GLPT) energy functional,[54] which has exactly the same form as a functional defined from the many-body perturbation theory (MBPT)[6, 55] and defines the OEP-GL2 method

$$\begin{aligned} E_c^{(2)} &= \frac{1}{2} \sum_{\sigma\tau} \sum_{ijab} \frac{|(i_{\sigma} a_{\sigma} | j_{\tau} b_{\tau})|^2}{\varepsilon_{i\sigma} + \varepsilon_{j\sigma} - \varepsilon_{a\tau} - \varepsilon_{b\tau}} \\ &\quad - \frac{1}{2} \sum_{\sigma\tau} \sum_{ijab} \frac{(i_{\sigma} a_{\sigma} | j_{\tau} b_{\tau})(i_{\sigma} b_{\sigma} | j_{\tau} a_{\tau})}{\varepsilon_{i\sigma} + \varepsilon_{j\sigma} - \varepsilon_{a\tau} - \varepsilon_{b\tau}} \\ &\quad + \sum_{\sigma} \sum_{ia} \frac{|f_{ia}^{\sigma}|^2}{\varepsilon_{i\sigma} - \varepsilon_{a\sigma}} \end{aligned} \quad (5)$$

with $f_{pq}^{\sigma} = \varepsilon_{p\sigma} \delta_{pq} - \langle p_{\sigma} | \hat{K} + v_{xc} | q_{\sigma} \rangle$ being the Fock matrix elements defined in terms of the KS spin orbitals. We also will present results for the OEP2-sc method, in which the KS orbitals undergo a semi-canonical transformation that makes the second-order energy expression

invariant with respect to orbital rotations (mixing of occupied or virtual orbitals among themselves).[8, 60].

For a given orbital- and eigenvalue-dependent XC energy functional (E_{xc}) the OEP equation for the XC KS potential can be written as [1, 3, 4, 6, 32, 33, 36]

$$\int X_{\sigma}(\mathbf{r}, \mathbf{r}') v_{xc,\sigma}^{\text{OEP}}(\mathbf{r}') d\mathbf{r}' = \Lambda_{xc,\sigma}(\mathbf{r}), \quad (6)$$

which is an integral equation (Fredholm of the first kind) with the inhomogeneity given by

$$\Lambda_{xc,\sigma}(\mathbf{r}) = \sum_p \left\{ \int \phi_{p\sigma}(\mathbf{r}) \sum_{q \neq p} \frac{\phi_{q\sigma}(\mathbf{r}) \phi_{q\sigma}(\mathbf{r}')}{\varepsilon_{p\sigma} - \varepsilon_{q\sigma}} \frac{\partial E_{xc}}{\partial \phi_{p\sigma}(\mathbf{r}')} d\mathbf{r}' + \frac{\partial E_{xc}}{\partial \varepsilon_{p\sigma}} |\phi_{p\sigma}(\mathbf{r})|^2 \right\} \quad (7)$$

where

$$X_{\sigma}(\mathbf{r}, \mathbf{r}') = 2 \sum_{ia} \frac{\phi_{i\sigma}(\mathbf{r}) \phi_{a\sigma}(\mathbf{r}) \phi_{i\sigma}(\mathbf{r}') \phi_{a\sigma}(\mathbf{r}')}{\varepsilon_{i\sigma} - \varepsilon_{a\sigma}}, \quad (8)$$

is the static KS linear response function. The explicit form of the OEP XC potential corresponding to the functionals of Eq. 4 and 5 can be found elsewhere [6, 8, 71, 83, 88] In practice, to solve the OEP equations Eq. (6) and calculate the OEP exchange and correlation potentials we employ the finite-basis set procedure, of Refs. [31, 34, 35, 74], which directly transforms the OEP equation into an algebraic problem. This is done by expanding the exchange and correlation potential and the KS linear response function Eq. (8) on an auxiliary, orthonormal, M-dimensional basis set $\{g_p(\mathbf{r})\}_{p=1}^M$ as

$$v_{xc,\sigma}^{\text{OEP}}(\mathbf{r}) = \sum_{p=1}^M c_p^{\sigma} g_p(\mathbf{r}), \quad (9)$$

and matrix representation of the response function reads

$$X_{\sigma}(\mathbf{r}, \mathbf{r}') = \sum_{pq} (\mathbf{X})_{pq,\sigma} g_p^*(\mathbf{r}) g_q(\mathbf{r}'), \quad (10)$$

where

$$\begin{aligned} (\mathbf{X})_{pq,\sigma} &= \int g_p^*(\mathbf{r}) X_{\sigma}(\mathbf{r}, \mathbf{r}') g_q(\mathbf{r}') d\mathbf{r}' d\mathbf{r} \\ &= \sum_{ia} \left(\frac{(ia|p)(ia|q)^*}{\varepsilon_i - \varepsilon_a} + c.c. \right), \end{aligned} \quad (11)$$

and

$$(rs|q) = \int d\mathbf{r}' \phi_s(\mathbf{r}') \phi_r^*(\mathbf{r}') g_q(\mathbf{r}').$$

is the overlap integral of the orbitals $\phi_s(\mathbf{r}')$, $\phi_r(\mathbf{r}')$ and the orthonormal auxiliary Gaussian function $g_q(\mathbf{r}')$. This step allows turning the solution of Eq. (6) into an algebraic problem in which the expansion coefficients (c_p) are obtained from the solution of OEP equation in the form

$$(\mathbf{X})_{qp,\sigma} c_p^{\sigma} = \mathbf{Y}_q, \quad (12)$$

and \mathbf{Y}_q is defined by the choice of the form of exchange and correlation functionals, e.g., OEPx, OEP-GL2, OEP2-sc. For the explicit expressions of \mathbf{Y}_q , see Refs. [6, 8, 60].

In addition, to ensure the correct $-1/r$ asymptotic behavior of the whole XC potential the Slater [89] or Fermi-Amaldi (FA) [90] potential is added to the $v_{xc,\sigma}^{\text{OEP}}$

$$v_{xc,\sigma}^{\text{OEP}}(\mathbf{r}) = v_{\text{Slater/FA}}^{\sigma}(\mathbf{r}) + \sum_{p=1}^M c_p^{\sigma} g_p(\mathbf{r}), \quad (13)$$

where the expansion coefficients c_p^{σ} are determined from the solution of the OEP equation Eq. (12).

In practice, the matrix representation of the response function \mathbf{X} is ill-conditioned[31, 74]. This is due to the fact that any functions orthogonal to the product functions $\phi_i(\mathbf{r})\phi_a(\mathbf{r})$ could be added to the expansion but should have zero weight in the OEP solution, forcing a computed zero with its numerical inaccuracies. To accommodate this, we use the singular-value decomposition (SVD) procedure to obtain the pseudoinverse of the density-density response matrix, $(\mathbf{X}^{-1})_{qp}$ [35, 69, 74]. That is achieved by the following two-step procedure. In the first step, the real symmetric matrix \mathbf{X} is diagonalized through an orthogonal transformation \mathbf{U} , i.e., $\mathbf{X} = \mathbf{U}\mathbf{\Omega}\mathbf{U}^{-1}$ where $\mathbf{\Omega}$ is a diagonal matrix that contains the ω_p eigenvalues and \mathbf{U} contains the eigenvectors. In the second step, the pseudoinverse is calculated by $\mathbf{X}^{-1} = \mathbf{U}\mathbf{\Omega}^{-1}\mathbf{U}^{-1}$ where each element of the diagonal $\mathbf{\Omega}^{-1}$ is the reciprocal $1/\omega_p$ of the corresponding eigenvalue when the eigenvalue is greater than a specified threshold (SVD cutoff) and is set to zero if the eigenvalue is smaller than or equal to the threshold. This replacement with zero eigenvalues, i.e., constant functions, from the representation given by Eq. (9).

This regularization is the critical aspect and an essential step in determining the stable solutions of the OEP equations in the finite-basis set representation.[8, 59, 69, 71]. Usually the SVD cutoff of 10^{-6} is chosen for LCAO OEP calculations to achieve a compromise between convergence and numerical stability.[29, 60, 71, 91]

III. COMPUTATIONAL DETAILS

All OEP calculations have been performed using locally modified ACES II package [92] where the finite-basis set implementation of OEP [34, 35, 74] is implemented.

As mentioned above, in most cases, we use the same basis set to represent both the orbitals and the XC OEP potential, which has been shown to give reasonable accuracy of results[93]. The only exception from that is made for two cases in Table I of the current work (rows denoted as cc-pVTZ/P1 and cc-pVTZ/P2) where we have performed the calculations using the identical computational setup as in Ref. 82 with auxiliary basis set taken from Table I of the aforementioned work. All details

about the basis set used in the present work are given in the text. As noted before, the numerical instability in the solution of OEP equations [31, 42, 60, 76, 77, 79–81, 83, 85] were minimized by employing a truncated SVD method for the construction of the pseudo-inverse of the linear response function in the OEP procedure. This regularization is an essential step in determining stable solutions of the OEP equation which in combination with the proper choice of basis set, ensures stable and physically sound solutions, avoiding in particular variational collapse observed in Ref. 82. Finally, we underline that in all LCAO OEP calculations, we have employed FA potential as a seed potential in Eq. (13) (N is a number of electrons).

$$v_{xc}^{FA}(\mathbf{r}) = -\frac{1}{N} \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (14)$$

Moreover, the tight convergence criteria were enforced in the KS-OEP procedure i.e., at the convergence point, the gradient of the total electronic energy with respect to variations of the c_p^σ coefficients in Eq. (13) was less than 10^{-9} . Finally, the cutoff for truncated SVD was set to 10^{-6} , and results were carefully checked to ensure convergence with respect to this parameter.

IV. RESULTS

To start our discussion, first in Tab. I, we report the results obtained for OEPx, OEP-GL2, and OEP2-sc for He atom and several basis sets listed in the first column of Tab. I. The second column contains the total energies (in Hartree, sign reversed) obtained within the given method with FA guiding potential (see Eq. (13)) and SVD regularization turned on. One can note that for these settings, all methods converged without problems, regardless of the utilized basis set. Additionally, we observe that at the OEPx level, we can converge to numerical results (2.8617 Ha) with the proper choice of basis set (UGBS[94] and 20S10P2D). This is not a surprising result, because the FA guiding potential provides the exact solution of the OEPx equation for this system. Thus, the remaining part of Eq. (13) is exactly zero. A similar situation can also be observed in the case of OEP-GL2 and OEP2-sc methods. In the former method, the results for the 20S10P2D and uncontracted aug-cc-pVQZ basis sets (2.9078 Ha and 2.9085 Ha) are in line with the numerical data (2.9099 Ha) from Ref. 66, showing the numerical stability of the LCAO OEP procedure. In turn, for OEP2-sc method for the 20S10P2D basis set gives almost the same total energy as in the case of the second-order Moller-Plesset method i.e., 2.8970 Ha. A similar situation was observed for the uncontracted aug-cc-pVQZ basis set. This behavior is not surprising for the He atom and was already observed in some studies[70–72]. One important fact to note is that the stable solution was also obtained for the basis

set reported in Table I of Ref. 82, which have been specially designed to recover near-degeneracy of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) in the case of OEP-GL2 method leading to a variational collapse of this methods. This is the first important finding of the present study, showing that with proper regularization, i.e. in our case, the truncated SVD, one can obtain physically meaningful OEP solutions.

The third column of Tab. I reports the total energy differences calculated concerning data in the second column for the case where the guiding FA potential is not included in the Eq. (13). Therefore, in this situation, the OEP procedure must fully catch the XC potential for a given orbital-dependent functional. One can note that for OEPx and OEP2-sc methods, the total energy difference error is exactly zero. Unfortunately, this is not the case for the OEP-GL2 method, where the error is between 10^{-5} Ha for the smallest basis set used and 10^{-9} Ha for the largest variant. This is traced back to the overestimation of the correlation effects in the OEP-GL2 method, which is even more pronounced with the lack of FA guiding potential. Nonetheless, these errors are sufficiently small at the convergence threshold for the largest basis set.

The fourth and fifth columns of Tab. I provide the same data for the case where SVD regularization of the density-density response matrix was switched off. In this situation, the convergence is only reached for the OEPx method with FA guiding potential. As was noted before, this is not surprising because the FA potential is the exact OEP solution for two-electron systems in the singlet state[95]. The neglect of the FA term leads to divergence of the OEPx method regardless of the basis set used. Again it confirms the necessity of using regularization in solving the LCAO OEP KS equations.

For the OEP-GL2 method with and without FA guiding potential, the results are diverging, being in line with the one reported in Ref. 82. One important fact to note here is that the variational collapse is observed in all basis sets we employed in our calculations. In the case of OEP2-sc, we observe similar behavior. In both cases, the calculations diverge. Although the construction of OEP2-sc is based on different choices of H_0 in second-order perturbation theory[8], it leads to the same numerical problems as the one encountered for the OEP-GL2 method when regularization of $(X_\sigma)_{pq}$ is omitted.

To conclude, we first note that to avoid variational collapse reported in the literature[82] of all tested OEP methods, one needs to employ the SVD regularization of the density-density response matrix. Secondly, to obtain OEP results that are close to their numerical counterparts, one needs to utilize a sufficiently large basis set.

To support the second conclusion we report in Tab. II the total energies obtained with numerical[66, 98] and LCAO OEP implementation[34, 35] for several closed- and open-shell atoms at OEPx and OEP-GL2 level of theory. In the case of LCAO OEP code, for the He atom,

TABLE I. The OEP results for the He atom as obtained using various basis sets and methods. The second column contains the total energies (in Ha, sign reversed) obtained within the given method with FA guiding potential and SVD regularization turned on. The third and following columns contain the total energy differences calculated concerning data in the second column.

Basis set	SVD=ON ^a		SVD=OFF ^b	
	FA	NONE	FA	NONE
	OEPx			
cc-pVTZ ^c	2.8612	0	0	diverge
cc-pVTZ/P1 ^d	2.8612	0	0	diverge
cc-pVTZ/P2 ^e	2.8612	0	0	diverge
aug-cc-pVQZ ^f	2.8615	0	0	diverge
UGBS ^g	2.8617	0	0	diverge
20S10P2D ^h	2.8617	0	0	diverge
	OEP-GL2			
cc-pVTZ	2.9052	10 ⁻⁵	diverge	diverge
cc-pVTZ/P1	2.9052	10 ⁻⁵	diverge	diverge
cc-pVTZ/P2	2.9052	10 ⁻⁶	diverge	diverge
aug-cc-pVQZ	2.9085	10 ⁻⁸	diverge	diverge
UGBS	2.8801	10 ⁻⁹	diverge	diverge
20S10P2D	2.9078	10 ⁻⁹	diverge	diverge
	OEP2-sc			
cc-pVTZ	2.8949	0	diverge	diverge
cc-pVTZ/P1	2.8949	0	diverge	diverge
cc-pVTZ/P2	2.8949	0	diverge	diverge
aug-cc-pVQZ	2.8976	0	diverge	diverge
UGBS	2.8752	0	diverge	diverge
20S10P2D	2.8970	0	diverge	diverge

^a the SVD cutoff was set to 10⁻⁶

^b the SVD procedure was omitted

^c uncontracted basis set from Ref. 96

^d uncontracted basis set from Ref. 96 was used for the orbitals and basis set from Table I of Ref. 82 (Potential 1) for representing the XC potential

^e uncontracted basis set from Ref. 96 was used for the orbitals and basis set from Table I of Ref. 82 (Potential 2) for the XC potential

^f uncontracted basis set from Ref. 97

^g universal gaussian basis set from Ref. 94

^h even-tempered basis set from Ref. 6

we have employed the aug-cc-pV6Z[99] basis set to solve OEP equations, whereas for Li and Be, we have used aug-cc-pCVQZ[100–102] basis set. For all other systems, we utilized the aug-cc-CV5Z[96, 103] basis set. In all cases, the basis sets were fully uncontracted to provide the best possible representation of KS orbitals and XC potential within the LCAO OEP procedure.

At the exchange-only level of theory (OEPx method), the agreement between both approaches is almost perfect. The mean absolute error (MAE) and mean absolute relative error (MARE) of the LCAO OEPx method calculated with respect to the numerical counterpart give MAE=0.1 mHa and MARE=0.002%, respectively. Moreover, the mean error (ME) shows that we always approach the numerical results from above, possibly meaning that at the complete basis set limit (CBS), we can approach the perfect correspondence of results. In the case

of the OEP-GL2 method, the situation is slightly worse. Here the MAE and MARE (computed w.r.t. OEP-GL2 numerical data) yield 5.1253 mHa and 0.0063%, respectively, meaning that the impact of the basis set used in the correlated OEP calculation is more pronounced. Thus the CBS limit is harder to achieve (confirmed by ME). Finally, we note that for all investigated atoms, the LCAO OEP-GL2 method converged without any significant problem. One exception is only for Be atom[8, 22, 66, 68], which due to its nature (quasi-degeneracy of (1s)²(2s)² and (1s)²(2p)² ground state configurations[104]), does not converge, oscillating around some local minima. This is a well-known fact, reported and discussed many times in the previous works[8, 22, 60, 66, 68, 70, 88].

TABLE II. Total ground-state energies (in Ha, sign reversed) obtained for a few atoms with the OEP-GL2 and OEPx methods. The bottom lines report the mean error (ME), mean absolute error (MAE), and mean absolute relative error (MARE) calculated with respect to numerical OEP-GL2 and OEPx data, respectively. The numerical OEP-GL2 results have been taken from Ref. 66 whereas numerical OEPx data have been generated using the exact code[98].

Atom	OEP-GL2		OEPx	
	Numerical	LCAO	Numerical	LCAO
He	2.9099	2.9097	2.8617	2.8617
Li	7.4818	7.4805	7.4325	7.4325
Be	14.6965	14.6948 ^a	14.5724	14.5724
N	54.6216	54.6206	54.4034	54.4032
Ne	129.0265	129.0223	128.5454	128.5452
Na	162.3195	162.3081	161.8566	161.8564
Mg	200.1286	200.1190	199.6116	199.6115
P	341.3382	341.3300	340.7150	340.7150
Ar	527.6608	527.6515	526.8122	526.8121
	ME[mHa]	-5.2153	ME[mHa]	-0.1000
	MAE[mHa]	5.2153	MAE[mHa]	0.1000
	MARE[%]	0.0063	MARE[%]	0.0002

^a From perturbative calculation based on the OEPx density.

To support our findings for the total energies, we also analyzed the quality of the ionization potentials obtained from our LCAO OEP KS calculations. In Tab. III, we report the ionization potentials (in Ha) obtained from the highest occupied molecular orbital (HOMO) orbital energies of the neutral atoms from numerical and LCAO implementations of OEPx and OEP-GL2 methods. The findings are very similar to the ones reported for total energies. Both OEP-GL2 and OEPx methods provide very close results to their numerical counterparts, yielding MAE of about 0.0599 Ha (MARE = 0.0109%) and 1.7323 Ha (MARE = 0.0063%), respectively. These results indirectly also confirm the quality of XC potentials obtained within the LCAO OEP procedure since the HOMO energy is very sensitive to the quality of the XC potential[63, 72, 105, 106]. We have to stress here, then in the case of the OEP-GL2 method, like in the OEPx method[31, 35, 107], the correlated HOMO

condition[72] must be incorporated to correct HOMO energies obtained within the LCAO OEP procedure.

TABLE III. Ionization potentials (in Ha) obtained from the HOMO orbital energies of the neutral atoms from OEP-GL2 and OEPx methods. The ME, MAE, and MARE are calculated with respect to numerical OEP-GL2 and OEPx data, respectively. The numerical OEP-GL2 results have been taken from Ref. 66 whereas numerical OEPx data have been generated using the exact code[98].

Atom	OEP-GL2		OEPx	
	Numerical	LCAO	Numerical	LCAO
He	0.893	0.892	0.918	0.918
Li	0.198	0.198	0.196	0.196
Be	0.367	0.359 ^a	0.309	0.309
N	0.499	0.499	0.571	0.571
Ne	0.656	0.655	0.851	0.851
Na	0.191	0.191	0.182	0.182
Mg	0.305	0.301	0.253	0.253
P	0.385	0.384	0.392	0.392
Ar	0.557	0.556	0.591	0.591

ME[mHa]	-1.7006	ME[mHa]	-0.0493
MAE[mHa]	1.7323	MAE[mHa]	0.0599
MARE[%]	0.0063	MARE[%]	0.0109

^a From perturbative calculation based on the OEPx density.

As the last point of our analysis, we investigate the convergence of the total energies of all investigated atoms with respect to the SVD cutoff parameter (the eigenvalues of density-density response matrix (see Eq. (11)) $\omega_p < 10^{-\text{SVD}_C}$ are set to zero). In Fig. 1 and Fig. 2, we report two representative examples for He and Mg atoms obtained in various uncontracted basis sets and with FA guiding potential. In the case of the He atom and OEPx method, the convergence is reached regardless of the SVD cutoff parameter since, as was noted, FA potentials can be considered as exact exchange potential for two-electron systems. One can also note that for sufficiently large basis sets (i.e., 20S10P2D and aug-cc-pV6Z), we can reach almost numerical accuracy (error less than 10^{-4} Ha). In the case of the OEP-GL2 method, in turn, for $\text{SVD}_C > 16$, the calculation diverges for uncontracted cc-pVTZ and 20S10P2D basis sets. Again this is the manifestation of the necessity of incorporating the SVD regularization in all LCAO OEP KS calculations.

For the Mg atom at OEPx and OEP-GL2 level of theory, the calculations diverge for $\text{SVD}_C > 5$ or 6 depending on the basis set used. This indicates that for a relatively small basis, the SVD regularization is essential to obtain a stable solution within the given basis set. In most cases, it is sufficient to remove from the density-density response matrix all eigenvalues below 10^{-6} . This value for the SVD cutoff parameter was already recommended in several studies[29, 31, 74]

A different situation is encountered for the He atom with the uncontracted aug-cc-pV6Z basis set, where stable convergence is reached up to $\text{SVD}_C = 20$. A similar situation occurs for the Mg atom with an uncontracted

FIG. 1. Total energy difference between numerical and LCAO OEP(x and GL2 respectively) data for He atom in the function of SVD cutoff parameter ($\omega_p < 10^{-\text{SVD}_C}$ are set to zero in density-density response matrix (see Eq. (11)). All basis sets are fully uncontracted.

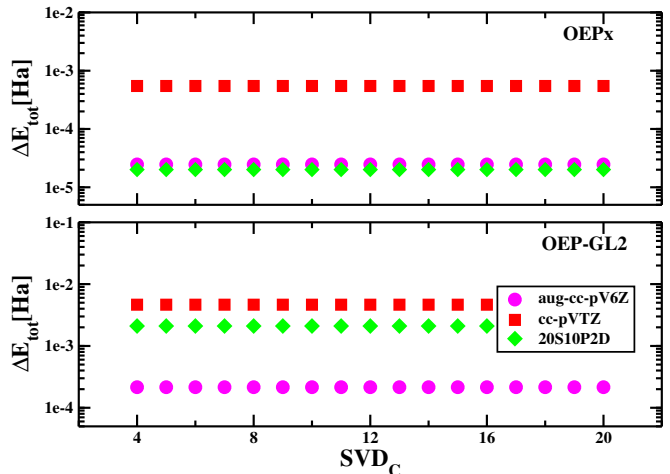
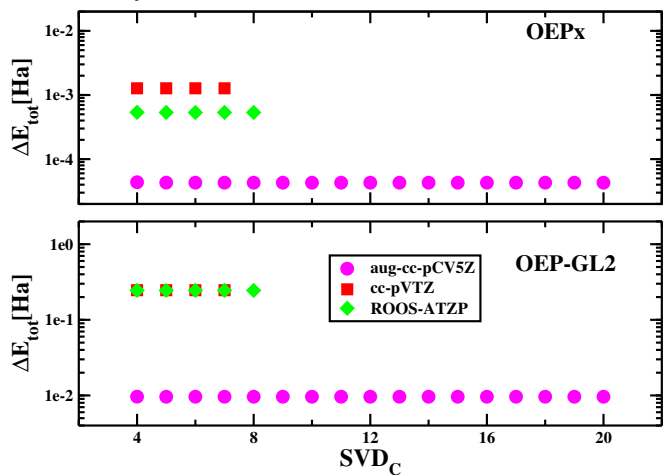


FIG. 2. Total energy difference between numerical and LCAO OEP(x and GL2 respectively) data for Mg atom in the function of SVD cutoff parameter ($\omega_p < 10^{-\text{SVD}_C}$ are set to zero in density-density response matrix (see Eq. (11)). All basis sets are fully uncontracted.



aug-cc-pCV5Z basis set. This might actually indicate that when the basis set is sufficiently large (close to the CBS limit), one can obtain a stable solution of the OEP method without employing any regularization procedure in the LCAO OEP calculations. This is a very interesting finding. To confirm this observation, we have performed the OEP calculations in the same basis set with switched-off regularization for the OEP-GL2 method obtaining the same results as previously.

V. CONCLUSIONS

By performing several finite basis set LCAO OEP calculations, for a set of atoms, we have shown that the physical solutions of the OEP equations in the context of KS-DFT at the exchange-only and correlation level, can be only obtained by employing the truncated SVD regularization procedure together with a proper choice of the basis sets. Regularization is the critical aspect in determining the stable and accurate solutions of the KS-OEP equations. And to obtain the OEP KS results that are close to their numerical counterparts, the utilization of a sufficiently large basis set is necessary. We have also shown that with this truncated SVD regularization we can avoid variational collapse reported in the literature [82] of all tested OEP methods. Finally, our results prove that LCAO OEP KS calculations can be safely used in test and routine applications.

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AUTHOR CONTRIBUTIONS

A.S. and V.K. contributed equally to this work.

DATA AVAILABILITY

The data that support the findings are published within this study.

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